



Aluminacyclopentanes in the synthesis of 3-substituted phospholanes and α,ω -bisphospholanes

Vladimir A. D'yakonov*, Alevtina L. Makhamatkhanova, Rina A. Agliullina, Leisan K. Dilmukhametova, Tat'yana V. Tyumkina and Usein M. Dzhemilev

Full Research Paper

Open Access

Address:
Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, Prospekt Oktyabrya, Ufa 450075, Russian Federation

Email:
Vladimir A. D'yakonov* - DyakonovVA@gmail.com

* Corresponding author

Keywords:
aluminacyclopentanes; Dzhemilev reaction; molybdenum complexes; phospholanes; zirconium complexes

Beilstein J. Org. Chem. **2016**, *12*, 406–412.
doi:10.3762/bjoc.12.43

Received: 14 December 2015
Accepted: 12 February 2016
Published: 02 March 2016

Associate Editor: J. P. Wolfe

© 2016 D'yakonov et al; licensee Beilstein-Institut.
License and terms: see end of document.

Abstract

An efficient one-pot process for the synthesis of 3-substituted phospholanes and α,ω -bisphospholanes was developed. The method involves the replacement of aluminium in aluminacyclopentanes, prepared in situ by catalytic cycloaluminum of α -olefins and α,ω -diolefins, by phosphorus atoms on treatment with dichlorophosphines ($R'PCl_2$). Hydrogen peroxide oxidation and treatment with S_8 of the synthesized phospholanes and α,ω -bisphospholanes afforded the corresponding 3-alkyl(aryl)-1-alkyl(phenyl)phospholane 1-oxides, 3-alkyl(aryl)-1-alkyl(phenyl)phospholane 1-sulfides, bisphospholane 1,1'-dioxides, and bisphospholane 1,1'-disulfides in nearly quantitative yields. The complexes $LMo(CO)_5$ ($L = 3$ -hexyl-1-phenylphospholane, 3-benzyl-1-methylphospholane, 1,2-bis(1-phenylphospholan-3-yl)ethane, and 1,6-bis(1-phenylphospholan-3-yl)hexane) were prepared by the reaction of 3-substituted phospholanes and α,ω -bisphospholanes with molybdenum hexacarbonyl. The structure of the complexes was proved by multinuclear 1H , ^{13}C , and ^{31}P spectroscopy.

Introduction

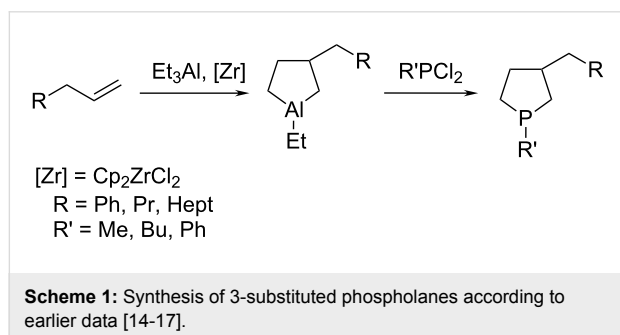
A widely used approach for the synthesis of cyclic organophosphorus compounds (OPC) is the direct transformation of five-membered metallocarbocycles based on transition metals to phosphacarbocycles on treatment with phosphorus dihalides. For example, a method for the direct conversion of zirconacyclopentenes [1-4] and zirconacyclopentadienes [5] to substituted phospholanes [6] and phospholes [7] has been reported.

This approach was used to obtain materials for light-emitting diodes (LEDs) [8], phosphorus-containing polymers [9,10], bisphospholes [11], bicyclodiphospholanes and spirobicyclodiphospholanes [12,13]. However, this method is faced with some practical complications related to the synthesis of the initial zirconacarbocycles: the reactions proceed at low temperatures (-78 °C) consuming stoichiometric amounts of expensive

Cp_2ZrCl_2 . In our opinion, the synthesis of cyclic OPC via catalytic cyclometallation reactions that we developed previously [14–17] would be free from the above-indicated drawbacks.

Furthermore, analysis of world literature demonstrated that the data on direct transformation of aluminacarbocycles [18] to cyclic OPCs are scarce, except for paper [19] in which this approach is implemented for simple olefins. Meanwhile, in our opinion, the development of these reactions would give rise to practically promising one-pot methods for the preparation of a broad range of cyclic and acyclic organophosphorus compounds of specified structure (phospholanes, phospholenes, phospholes and 1,2- and 1,4-diphosphorus compounds) that were difficult to synthesize or unknown before. In order to fill this gap and to extend the scope of applicability of the catalytic cycloaluminum of unsaturated compounds, we continued studies along this line, which form the subject of this paper.

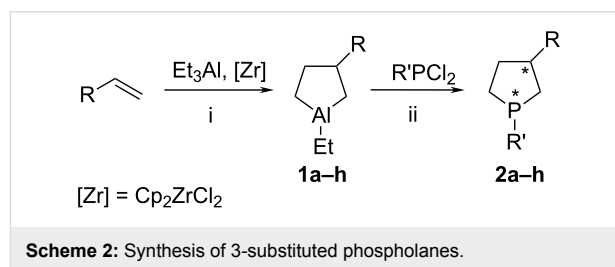
Previously [19], it was shown for allylbenzene, hex-1-ene, and oct-1-ene that aluminacyclopentanes, prepared by the reaction of these alkenes with Et_3Al in the presence of 5 mol % Cp_2ZrCl_2 (20 °C, 6–8 h), react in situ with $\text{R}'\text{PCl}_2$ ($\text{R} = \text{Me}, \text{Ph}$) in toluene for 30 min with replacement of the Al atom by a P atom to give the respective phospholanes in 79–84% yields (Scheme 1).



The present paper reports the results of experimental studies that further develop the earlier investigation about the substitution of phosphorus atoms for the Al atoms in aluminacyclopentanes with the goal to develop a preparative method for the synthesis of five-membered cyclic organophosphorus compounds.

Results and Discussion

First, we studied the effect of the structure of substituent in position 3 of the initial aluminacyclopentanes on the yield of target phospholanes. Under the selected conditions (toluene, 20–22 °C, 30 min), 3-alkyl-substituted aluminacyclopentanes **1a–c** react with phenyldichlorophosphine to give 3-butyl-1-phenylphospholane (**2a**), 3-hexyl-1-phenylphospholane (**2b**), or 3-octyl-1-phenylphospholane (**2c**) in ca. 92, 91, and 87% yields, respectively (Scheme 2, Table 1). The isolated organophosphorus compounds **2a–c** are 3:2 mixtures of diastereomers formed due to the presence of two asymmetric centres in the molecule at C-3 and P-1. The latter exists due to the high barrier for inversion of configuration at the phosphorus atom [20].



The diastereomeric mixture was identified by multinuclear ^1H , ^{13}C , and ^{31}P NMR spectroscopy and conventionally designated as the *syn* and *anti* isomers in which, for example, the high-priority substituents at P-1 and C-3 are proximate in the *syn* isomer. Using the homo- and heteronuclear 2D NMR spectroscopy (H,H-COSY , HSQC , HMBC), parameters of the NMR spectra of some compounds **2** were determined and proved to

Table 1: Results of 3-substituted phospholanes ^a.

Entry	R	R'	Product	Yield (%)	<i>trans/cis</i>
1	Bu	Ph	2a^b	92	3/2
2	Hex	Ph	2b	91	3/2
3	Oct	Ph	2c	87	3/2
4	cyclohexyl	Ph	2d	93	3/2
5	cyclohexen-3-yl	Ph	2e	90	3/2
6	Bn	Ph	2f^b	82	3/2
7	Bn	Me	2g^b	84	2/1
8	Bn	Bu	2h	86	2/1

^aReaction conditions: (i) 10 mmol Et_3Al , 5 mol % Cp_2ZrCl_2 , toluene (25 mL), room temperature, 12 hours; (ii) 10 mmol $\text{R}'\text{PCl}_2$, –5 °C to room temperature, 30 minutes. ^bThe cyclic OPCs have been previously synthesized and described in [19].

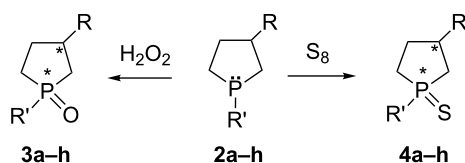
agree with published data [19]. Specifically, 1-phenyl-3-substituted phospholanes typically show ^{31}P NMR signals in area of -14 to -13 ppm, except for the 1-alkyl-3-benzylphospholane **2g** and **2h** isomers, for which the signals occur at $\delta_{\text{P}} = -34$ ppm and -35 ppm, and -22 to -23 ppm, respectively. The presence of a magnetically active phosphorus atom in the five-membered heterocycle induces the doublet splitting of the carbon signals in the ^{13}C NMR spectra of **2a–h** for both the P-substituent and the ring. The highest heteronuclear constants $J(^{31}\text{P}^{13}\text{C})$ for the ring, $^1J_{\text{PC}} \approx 10\text{--}20$ Hz, are found for the α -carbon atoms (C-2 and C-5) of phospholanes **2a–h**.

Allylbenzene reacts with AlEt_3 (5 mol % Cp_2ZrCl_2 , 20°C , 12 h) to give 3-benzyl-1-ethylaluminacyclopentane **1f**, which then reacts with phenyldichlorophosphine giving rise to 3-benzyl-1-phenylphospholane **2f** in a yield of 82% (Scheme 2).

When PhPCl_2 is replaced by MePCl_2 or BuPCl_2 , the reaction with 3-benzyl-1-ethylaluminacyclopentane **1f** affords the corresponding phospholanes **2g,h** with one of the isomers predominating (Table 1).

In the case of 3-cyclohexyl- and 3-(cyclohex-3-en-1-yl)-1-phenylphospholanes (**2d** and **2e**), the number of stereoisomers increases owing to the additional asymmetric centre C(1') in the substituent, and the total yield of these compounds is 90–93%.

Phospholanes **2a–h** readily react with H_2O_2 in chloroform, owing to the presence of a lone electron pair at phosphorus to give phospholane 1-oxides **3a–h** in quantitative yields. The reaction of **2a–h** with S_8 affords phospholane 1-sulfides **4a–h** also in quantitative yields (Scheme 3).



Scheme 3: Synthesis of 3-substituted phospholane oxides and sulfides.

In the ^{31}P NMR spectra of phospholane oxides **3a–h** and phospholane sulfides **4a–h**, the phosphorus signal shifts downfield to ca. $57\text{--}70$ ppm relative to the initial phospholanes, and the heteronuclear constants $^1J(^{31}\text{P}^{13}\text{C}_2)$ and $^1J(^{31}\text{P}^{13}\text{C}_5)$ observed in the ^{13}C NMR spectra increase to ca. $53\text{--}66$ Hz.

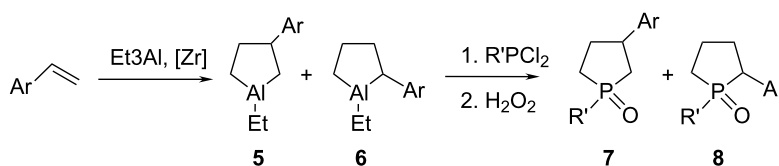
When styrene or 2-vinylnaphthalene reacts with AlEt_3 in the presence of Cp_2ZrCl_2 , apart from 3-phenyl(naphthyl)-1-ethylaluminacyclopentanes **5a–f**, the reaction mixture contains 2-phenyl(naphthyl)-1-ethylaluminacyclopentane **6a–f** [21]. Both regioisomers react in situ with phosphorus dihalides and hydrogen peroxide to afford 1-phenyl(alkyl)-2-arylphospholane oxides **7a–f** and 1-phenyl(alkyl)-3-arylphospholane oxides **8a–f** in 2:1 ratio in a 69–87% total yield (Table 2). The regioisomers were isolated by column chromatography (hexane/ethyl acetate/methanol = 5:3:1) and characterized in a separate fraction (Scheme 4).

Table 2: Results of 3-substituted and 2-substituted phospholanes.

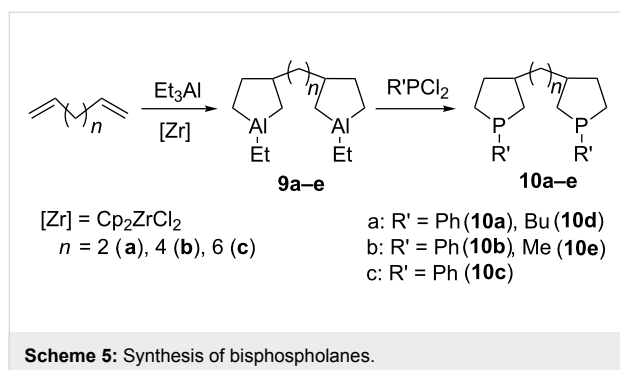
Entry	Ar	R'	Product	Ratio	Yield (%)
1	Ph	Me	7a, 8a	2/1	84
2	Ph	Bu	7b, 8b	2/1	87
3	Ph	<i>t</i> -Bu	7c, 8c	2/1	81
4	Ph	Ph	7d, 8d	2/1	75
5	Naphtyl	Me	7e, 8e	2/1	72
6	Naphtyl	Ph	7f, 8f	2/1	69

It should be noted that the phosphorus signals of major intensity of 2-aryl phospholane oxides **8a, 8b, 8d, 8e, 8f**, corresponding to one of the stereoisomers, are shifted upfield by ca. $5\text{--}7$ ppm with respect to those of 3-aryl-substituted phospholane oxides **7**. In contrast, the ^{31}P NMR signal of the second isomer of **8** is shifted to lower field.

For further development of this study, it appeared pertinent to apply our method in the preparation of α,ω -bisphospholane compounds by the reaction of phosphorus dihalides with bisaluminacyclopentanes (Scheme 5).



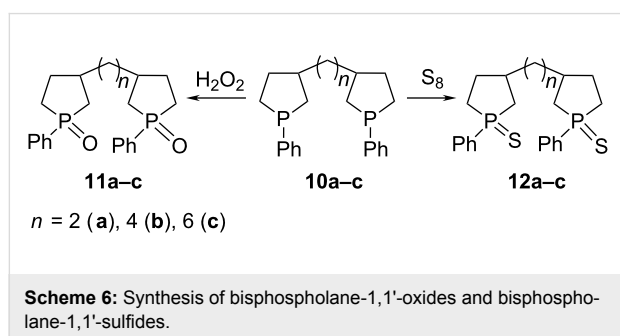
Scheme 4: Synthesis of 3-substituted **7a–f** and 2-substituted **8a–f** phospholanes.



Thus bisaluminacyclopentane **9a**, synthesized by catalytic cycloalumination of 1,7-octadiene, was subjected without isolation to the substitution reaction with aryl(alkyl)dichlorophosphine with replacement of Al by P (ca. 20 °C, 30 min) to give bisphospholane **10a** as a mixture of isomers in a total yield of 84–85%.

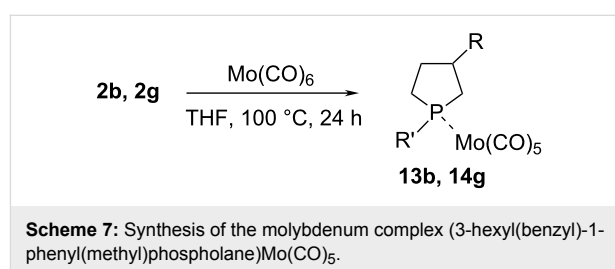
Under the selected conditions, bisaluminacyclopentanes **9b–e**, prepared by catalytic cycloalumination of 1,5-hexadiene and 1,9-decadiene, react with phenyl(methyl, butyl)dichlorophosphine to give 1,2-bis(1-phenylphospholan-3-yl)ethane (**10b**), 1,2-bis(1-butylphospholan-3-yl)ethane (**10d**), 1,4-bis(1-methylphospholan-3-yl)butane (**10e**), and 1,6-bis(1-phenylphospholan-3-yl)hexane (**10c**) in 85 % yields.

Similarly to phospholanes **2a–h**, the resulting bisphospholanes **10a–c** readily react with H₂O₂ in chloroform or with elemental sulfur to furnish the corresponding bisphospholane 1,1'-dioxides **11a–c** and bisphospholane 1,1'-disulfides **12a–c** (Scheme 6).

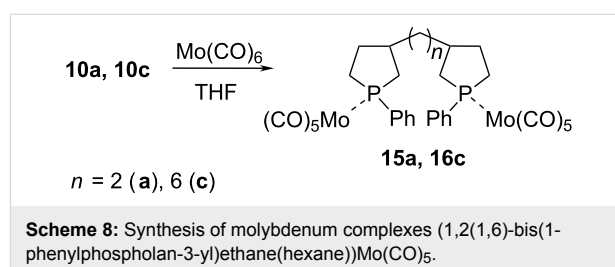


Diastereomeric cleavage of signals in the ¹³C NMR spectra of bisphospholanes observed only for compounds **10a**, **10d**, **11a**, **12a** in which the phospholane moieties are linked by two methylene groups, obviously as a result of mutual influence of the proximate asymmetric centres at C-3 and C-3'. Ratios of stereoisomers were determined by HPLC method as 2:1 (see Supporting Information File 2, Figure S1).

Organophosphorus compounds, including cyclic ones, are known to readily form complexes with transition metals, which are extensively studied and used in homogeneous catalytic reactions. Therefore, in order to study the properties of the cyclic OPC that we prepared and to demonstrate how they could be used as ligands, we investigated the reaction of 3-substituted phospholanes and bisphospholanes with Mo(CO)₆, resulting in the preparation of molybdenum complexes. For example, 3-hexyl-1-phenylphospholane and 3-benzyl-1-methylphospholane react with Mo(CO)₆ furnishing molybdenum complexes **13b** and **14g** (Scheme 7).



The complex formation is evidenced by changes in the NMR spectral parameters of compounds **13b** and **14g** in relation to the initial phospholanes. A typical feature is the downfield shift of the ³¹P NMR signals. As a result, both compounds were found to exhibit close chemical shifts δ_P ≈ 25 ppm and δ_P ≈ 26 ppm for the diastereomers formed, irrespective of the nature of substituent R', which is indicative of equal pyramidity of the bonds of the phosphorus atom incorporated in the molybdenum complex. In addition, the C-5 signal in the ¹³C NMR spectra is shifted downfield by ca. 8 ppm and the constant J_{PC5} = 24.1 Hz (for example, for **13b**) is much higher not only compared to the corresponding atom in the initial phospholane **2b** but also than J_{PC2} = 3.0 Hz in compound **13b**. In view of the fact that the phosphorus–carbon constants obey the Karplus equation [22], this result suggests that the conformation of the five-membered heterocycle changes upon the formation of the complex with molybdenum hexacarbonyl. Similarly, bisphospholanes **10a** and **10c** react with Mo(CO)₆ to form molybdenum complexes **15a** and **16c** (Scheme 8). The resulting molybdenum complexes are oily liquids. The structure of the complexes was also proved by spectral data.



Conclusion

Thus, as a continuation of investigations dealing with the search for effective methods for the synthesis of five-membered cyclic organophosphorus compounds, we developed a preparative process for the one-pot conversion of aluminacyclopentanes, obtained in situ by catalytic cycloaluminum of olefins or diolefins with AlEt_3 , to phospholanes, phospholane oxides or phospholane sulfides, including bisphospholanes and their derivatives in high yields.

The developed methods are distinguished by easy implementation of the reaction with the use of accessible reagents and monomers, which makes them quite promising for the use in both the laboratory practice and industry.

Experimental

Preparation of 3-alkyl(aryl)phospholanes (general procedure)

A glass reactor maintained under dry argon at 0 °C was successively charged, with stirring, with toluene (25 mL), Cp_2ZrCl_2 (0.298 g, 1 mmol), olefin (10 mmol), and AlEt_3 (1.8 mL, 10 mmol). The mixture was warmed up to room temperature (ca. 20 °C) and stirred for 12 h. Then the reaction mixture was cooled down to –5 to –10 °C, alkyl(phenyl)dichlorophosphine (10 mmol) was added dropwise, and the mixture was stirred at room temperature for additional 30 min. Then the reaction mixture was treated with a saturated aqueous solution of NH_4Cl and the reaction products were extracted with diethyl ether and dried with MgSO_4 . The solvent was evaporated and the target phospholanes were isolated by vacuum distillation. All operations were carried out in an argon flow.

The general procedure and analytical data for compounds **2a**, **2b**, **2f**, **2g** and **3a**, **3b**, **3f**, **3g** were previously described in [19].

3-Octyl-1-phenylphospholane (**2c**) in the mixture in a ratio of 3:2: Colorless oil (87%); bp 215–218 °C (9 torr); calcd for $\text{C}_{18}\text{H}_{29}\text{P}$: C, 78.22%; H, 10.58%; found: C, 78.3%; H, 10.6%; ^1H NMR (400.13 MHz, CDCl_3) δ 0.95 (t, $^3J = 6.8$ Hz, 6H, C(8')H), 1.27–1.63 (m, 32H, C(1')H, C(2')H, C(3')H, C(4')H, C(5')H, C(6')H, C(7')H, C(4)H_a, C(2)H_a), 1.94–2.03 (m, 4H, C(3)H, C(5)H_a), 2.10–2.20 (m, 4H, C(2)H_b, C(4)H_b), 2.26 (m, 2H, C(5)H_b), 7.24–7.30, 7.32–7.38, 7.42–7.48 (m, 10H, Ph); ^{13}C NMR (100.62 MHz, CDCl_3) δ 14.15 (C(8')), 22.70 (C(7')), 25.79 ($J_{\text{PC}} = 12.1$ Hz, C(5)), 26.60 ($J_{\text{PC}} = 10.1$ Hz, C(5)), 28.49, 28.61 (C(2')), 29.04, 29.05 (C(4')), 29.32 (C(5')), 29.57, 29.64 (C(3')), 31.63 (C(6')), 32.92 ($J_{\text{PC}} = 13.1$ Hz, C(2)), 33.16 ($J_{\text{PC}} = 11.1$ Hz, C(2)), 33.95 ($J_{\text{PC}} = 3.0$ Hz, C(4)), 34.24 ($J_{\text{PC}} = 4.0$ Hz, C(4)), 35.60 ($J_{\text{PC}} = 3.0$ Hz, C(1')), 35.86 ($J_{\text{PC}} = 5.0$ Hz, C(1')), 41.82 ($J_{\text{PC}} = 4.0$ Hz, C(3)), 43.02 ($J_{\text{PC}} = 1.0$ Hz, C(3)), 126.87 (C(9)), 127.90, 127.91 ($J_{\text{PC}} = 5.0$ Hz, C(8), C(10)),

130.07 ($J_{\text{PC}} = 16.1$ Hz, C(7), C(11)), 130.13 ($J_{\text{PC}} = 15.1$ Hz, C(7), C(11)), 142.47, 142.84 ($J_{\text{PC}} = 23.1$ Hz, C(6)) (P-Ph); ^{31}P NMR (161.97 MHz, CDCl_3) δ –13.5, –13.9; MALDI–TOF: m/z calcd for $\text{C}_{18}\text{H}_{30}\text{P}$ ($[\text{M} + \text{H}]^+$): 277.4046; found: 277.4.

Preparation of 3-alkyl(aryl)phospholane-1-oxides (general procedure)

A 30% solution of hydrogen peroxide (0.7 mL, 6 mmol) was slowly added dropwise with vigorous stirring to a solution of 3-alkyl(benzyl)-1-alkyl(phenyl)phospholane (5 mmol), synthesized as described above, in chloroform (10 mL) and the mixture was stirred for 1 h. Then the reaction mixture was washed with water (3 × 5 mL) and the organic layer was dried with MgSO_4 . The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate/methanol 5:3:1). 3-Octyl-1-phenylphospholane-1-oxide (**3c**) in the mixture in a ratio of 3:2: Calcd for $\text{C}_{18}\text{H}_{29}\text{OP}$: C, 73.94; H, 10.00%; found: C, 73.7%; H, 9.8%; ^1H NMR (400.13 MHz, CDCl_3) δ 0.81 (t, $^3J = 7.2$ Hz, 6H, C(8')H), 1.17–1.60 (m, 30H, C(2)H_a, C(4)H_a, C(1')H, C(2')H, C(3')H, C(4')H, C(5')H, C(6')H, C(7')H), 1.70 (m, 1H, C(2)H_a), 1.80 (m, 1H, C(4)H_a), 1.87 (m, 1H, C(5)H_a), 1.94–2.12 (m, 2H, C(3)H, C(5)H_a), 2.14–2.35 (m, 7H, C(2)H_b, C(3)H, C(4)H_b, C(5)H_b), 7.36–7.56, 7.60–7.78 (m, 10H, Ph); ^{13}C NMR (100.62 MHz, CDCl_3) δ 13.82 (C(8')), 22.35 (C(7')), 27.51, 27.60 (C(2')), 28.94, 28.96 (C(4')), 29.19 ($J_{\text{PC}} = 66.4$ Hz, C(5)), 29.21 (C(5')), 29.32, 29.36 (C(3')), 30.18 ($J_{\text{PC}} = 66.4$ Hz, C(5)), 30.99 ($J_{\text{PC}} = 6.0$ Hz, C(4)), 31.55 (C(6')), 31.93 ($J_{\text{PC}} = 7.0$ Hz, C(4)), 35.87 ($J_{\text{PC}} = 55.3$ Hz, C(2)), 35.99 ($J_{\text{PC}} = 12.1$ Hz, C(1')), 36.04 ($J_{\text{PC}} = 14.1$ Hz, C(1')), 36.16 ($J_{\text{PC}} = 53.3$ Hz, C(2)), 38.60, 40.21 ($J_{\text{PC}} = 8.0$ Hz, C(3)), 128.39 ($J_{\text{PC}} = 12.1$ Hz, C(8), C(10)), 129.55 ($J_{\text{PC}} = 10.1$ Hz, C(7), C(11)), 131.40 ($J_{\text{PC}} = 3.0$ Hz, C(9)), 133.90 ($J_{\text{PC}} = 89.5$ Hz, C(6)), 134.00 ($J_{\text{PC}} = 90.5$ Hz, C(6)) (P-Ph); ^{31}P NMR (161.97 MHz, CDCl_3) δ 59.7, 59.4; MALDI TOF: m/z calculated for $\text{C}_{18}\text{H}_{30}\text{OP}$ ($[\text{M} + \text{H}]^+$): 293.4040; found: 293.5.

General procedure for the preparation of 3-alkyl(aryl)phospholane-1-sulfides

Reactions were performed under argon. Sulfur (0.13 g, 4 mmol) was added with cooling to a solution of 3-alkyl(aryl)phospholane (4 mmol) (prepared as described above) in 10 mL toluene, and the mixture was stirred for 4 h. After filtration through a thin layer of silica gel the solvent was evaporated to give a colorless oil. 3-Hexyl-1-phenylphospholane-1-sulfide (**4b**) in the mixture in a ratio of 3:2: Calculated for $\text{C}_{16}\text{H}_{25}\text{PS}$: C, 68.53%; H, 8.99%; found: C, 68.4%; H, 8.0%; ^1H NMR (400.13 MHz, CDCl_3) δ 0.91 (t, $^3J = 6.8$ Hz, 6H, C(6')H), 1.25–1.43 (m, 16H, C(2')H, C(3')H, C(4')H, C(5')H), 1.43–1.61 (m, 5H, C(1')H, C(4)H_a), 1.83–1.95 (m, 2H, C(2)H_a, C(4)H_a), 1.99 (m, 1H, C(2)H_a), 2.11–2.52 (m, 8H, C(2)H_b, C(3)H, C(4)H_b, C(5)H_a, C(5)H_b), 2.60 (m, 1H, C(5)H_b), 2.66 (m, 1H,

C(2)H_b), 7.42–7.53, 7.82–7.94 (m, 10H, Ph); ¹³C NMR (100.62 MHz, CDCl₃) δ 13.77 (C(6')), 22.27, 22.29 (C(5')), 27.62, 27.68 (C(2')), 29.00 (C(3')), 31.41, 31.43 (C(4')), 31.86 (*J*_{PC} = 6.0 Hz, C(4)), 33.62 (*J*_{PC} = 4.0 Hz, C(4)), 35.44 (*J*_{PC} = 14.1 Hz, C(1')), 35.64 (*J*_{PC} = 53.3 Hz, C(5)), 35.71 (*J*_{PC} = 12.1 Hz, C(1')), 36.49 (*J*_{PC} = 53.3 Hz, C(5)), 39.74 (*J*_{PC} = 8.0 Hz, C(3)), 41.78 (*J*_{PC} = 6.0 Hz, C(3)), 41.94 (*J*_{PC} = 54.3 Hz, C(2)), 42.38 (*J*_{PC} = 53.3 Hz, C(2)), 128.30 (*J*_{PC} = 12.1 Hz, C(8), C(10)), 130.00 (*J*_{PC} = 11.1 Hz, C(7), C(11)), 131.07 (*J*_{PC} = 2.0 Hz, C(9)), 133.76, 133.84 (*J*_{PC} = 70.4 Hz, C(6)) (P-Ph); ³¹P NMR (161.97 MHz, CDCl₃) δ 57.72; MALDI TOF: *m/z* calculated for C₁₆H₂₆P₂ ([M + H]⁺): 281.4174; found: 281.3.

General procedure for the preparation of Mo complexes **13b**, **14g**

Reactions was performed under argon using standard Schlenk techniques. A mixture of Mo(CO)₆ (0.79 g, 3 mmol) and 3-hexyl(benzyl)-1-phenyl(methyl)phospholane **2b**, **2g** (3 mmol) was stirred under reflux in 15 mL THF for 24 h. The colorless solution became dark-brown during this time. The solvent was removed under vacuum and the residue was chromatographed on silica gel (hexane). The product was obtained as dark green thick liquid. (3-Hexyl-1-phenylphospholane)pentacarbonylmolybdenum (**13b**) in the mixture in a ratio of 1:1: Calcd for C₂₁H₂₅MoO₅P: C, 52.08%; H, 5.20%; found: C, 52.2%; H, 5.3%; ¹H NMR (400.13 MHz, CDCl₃) δ 0.20–1.01 (s, 6H, C(6')H), 1.30–1.56 (s, 20H, C(5')H, C(3')H, C(2')H, C(4')H, C(1')H), 1.58–1.64 (m, 2H, C(4)H), 1.72–1.82 (m, 1H, C(2)H_a), 1.93–2.02 (m, 1H, C(3)H), 2.06–2.27 (m, 4H, C(4)H_b, C(2)H_b, C(3)H), 2.41–2.57 (m, 3H, C(5)H_a, C(5)H_b), 2.58–2.80 (m, 3H, C(5)H_b, C(2)H_a, C(2)H_b), 7.23–7.26, 7.31–7.33, 7.37–7.44, 7.45–7.56 (m, 10H, Ph); ¹³C NMR (100.62 MHz, CDCl₃) δ 14.10 (C(6')), 22.66, 22.72 (C(5')), 28.39, 28.42 (C(3')), 29.37, 29.44 (C(2')), 31.45 (*J*_{PC} = 22.1 Hz, C(5)), 31.81 (C(4')), 32.16 (*J*_{PC} = 24.1 Hz, C(5)), 33.42, 34.13 (C(4)), 35.70 (*J*_{PC} = 8.0 Hz, C(1')), 35.75 (*J*_{PC} = 9.1 Hz, C(1')), 38.19 (C(2)), 38.41 (*J*_{PC} = 3.0 Hz, C(2)), 41.78 (*J*_{PC} = 1.0 Hz, C(3)), 42.30 (C(3)), 128.81, 128.88 (*J*_{PC} = 10.1 Hz), 128.95 (*J*_{PC} = 11.1 Hz), 129.08, 139.67 (*J*_{PC} = 27.2 Hz, C(6)), 140.24 (*J*_{PC} = 28.2 Hz, C(6)) (P-Ph), 205.75 (*J*_{PC} = 9.1 Hz, CO_{cis}), 205.77 (*J*_{PC} = 9.1 Hz, CO_{cis}), 210.51 (*J*_{PC} = 22.1 Hz, CO_{trans}), 210.57 (*J*_{PC} = 21.1 Hz, CO_{trans}); ³¹P NMR (161.97 MHz, CDCl₃): δ 26.00, 25.20.

General procedure for the preparation of Mo complexes **15a**, **16c**

Reactions were performed under argon using standard Schlenk techniques. A mixture of Mo(CO)₆ (0.79 g, 3 mmol) and 1,2(1,6)-bis(1-phenylphospholan-3-yl)ethane(hexane) **10a**, **10c** (3 mmol) was stirred under reflux in 15 mL THF for 24 h. The colorless solution became brown during this time. The solvent was removed under vacuum and the crude product was purified

by silica gel column chromatography (hexane) giving a dark brown, thick liquid. 1,2-Bis(1-pentacarbonylmolybdenum-1-phenylphospholan-3-yl)ethane (**15a**) as a mixture of isomers. Calcd for C₃₂H₂₈Mo₂O₁₀P₂: C, 46.51%; H, 3.42%; found: C, 46.5%; H, 3.5%; ¹H NMR (400.13 MHz, CDCl₃) δ 1.28–1.39 (m, 2H, C(4)H_a, C(4)H_b), 1.40–1.60 (m, 2H, C(4)H_a, C(4)H_b), 1.64–1.73 (m, 1H, C(2)H_a), 1.84–1.94 (m, 1H, C(3)H), 1.98–2.22 (m, 6H, C(6'), C(2)H_b, C(3)H), 2.35–2.58 (m, 3H, C(5)H_a, C(5)H_b, C(2)H_a), 2.60–2.70 (m, 3H, C(5)H_a, C(5)H_b, C(2)H_b), 7.34–7.56 (m, 10H, P-Ph); ¹³C NMR (100.62 MHz, CDCl₃) δ 31.29, 31.35 (*J*_{PC} = 23.1 Hz, C(5)), 32.01 (*J*_{PC} = 23.1 Hz, C(5)), 32.05 (*J*_{PC} = 24.1 Hz, C(5)), 33.35, 33.40, 34.13, 34.17, 34.22 (C(4)), 34.37, 34.44, 34.52, 34.59 (C(6')), 38.31, 38.35, 38.37 (*J*_{PC} = 23.1 Hz, C(2)), 38.50, 38.54 (C(2)), 41.74, 41.82, 41.91, 42.36, 42.42 (C(3)), 128.84, 128.94, 129.03, 129.19, 139.44, 140.11 (*J*_{PC} = 28.2 Hz, C(6)) (P-Ph), 205.74, 205.83 (CO_{cis}), 210.49, 210.55 (*J*_{PC} = 22.1 Hz, CO_{trans}); ³¹P NMR (161.97 MHz, CDCl₃) δ 25.3, 26.3.

Supporting Information

Detailed synthesis and characterization procedures are provided for all compounds synthesized and characterized. NMR spectra are provided for all compounds for which NMR data are reported.

Supporting Information File 1

Experimental details, characterization data of all products.
[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-43-S1.pdf>]

Supporting Information File 2

NMR spectra.
[<http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-12-43-S2.pdf>]

Acknowledgements

This work was supported financially by the Russian Foundation for Basic Research (Grants 15-33-20043, 16-33-00193). The HPLC analysis was performed with equipment at the Center for the Collective Use “Chemistry” of the Ufa Institute of Chemistry of the Russian Academy of Sciences.

References

- Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310–2312. doi:10.1021/ja00215a057
- Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880–1889. doi:10.1021/ja00084a031
- Hydro, J.; Gouyguo, M.; Dallemer, F.; Daran, J.-C.; Balavoine, G. G. A. *J. Organomet. Chem.* **2000**, *595*, 261–267. doi:10.1016/S0022-328X(99)00635-X

4. Zhou, Y.; Wang, S.; Chen, C.; Xi, C. *RSC Adv.* **2015**, *5*, 71724–71727. doi:10.1039/C5RA13818C
5. Crassous, J.; Réau, R. *Dalton Trans.* **2008**, 6865–6876. doi:10.1039/b810976a
6. Zhou, Y.; Yan, X.; Xi, C. *Tetrahedron Lett.* **2010**, *51*, 6136–6138. doi:10.1016/j.tetlet.2010.09.061
7. Hu, G.; Zhang, Y.; Su, J.; Li, Z.; Gao, Y.; Zhao, Y. *Org. Biomol. Chem.* **2015**, *13*, 8221–8231. doi:10.1039/C5OB00959F
8. Fave, C.; Hissler, M.; Kárpáti, T.; Rault-Berthelot, J.; Deborde, V.; Toupet, L.; Nyulászai, L.; Réau, R. *J. Am. Chem. Soc.* **2004**, *126*, 6058–6063. doi:10.1021/ja0317067
9. Mao, S. S. H.; Tilley, T. D. *Macromolecules* **1997**, *30*, 5566–5569. doi:10.1021/ma9701402
10. Makhamatkhanova, A. L.; Dil'mukhametova, L. K.; Tyumkina, T. V.; D'yakonov, V. A.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2013**, *62*, 2467–2471. doi:10.1007/s11172-013-0357-x
11. Doherty, S.; Eastham, G. R.; Tooze, R. P.; Scanlan, T. H.; Williams, D.; Elsegood, M. R. J.; Clegg, W. *Organometallics* **1999**, *18*, 3558–3560. doi:10.1021/om990346m
12. Mirza-Aghayan, M.; Boukherroub, R.; Etemad-Moghadam, G.; Manuel, G.; Koenig, M. *Tetrahedron Lett.* **1996**, *37*, 3109–3112. doi:10.1016/0040-4039(96)00503-5
13. Oba, G.; Phok, S.; Manuel, G.; Koenig, M. *Tetrahedron* **2000**, *56*, 121–127. doi:10.1016/S0040-4020(99)00780-2
14. Dzhemilev, U. M.; Ibragimov, A. G. *J. Organomet. Chem.* **2010**, *695*, 1085–1110. doi:10.1016/j.jorganchem.2010.01.002
15. Dzhemilev, U. M.; D'yakonov, V. A. Hydro-, Carbo- and Cycloaluminum of Unsaturated Compounds. In *Modern Organoaluminum Reagents: Preparation, Structure, Reactivity and Use*; Woodward, S.; Dagorne, S., Eds.; Springer: Berlin, Heidelberg, 2013; Vol. 41, pp 312 ff.
16. D'yakonov, V. A.; Trapeznikova, O. A.; de Meijere, A.; Dzhemilev, U. M. *Chem. Rev.* **2014**, *114*, 5775–5814. doi:10.1021/cr400291c
17. D'yakonov, V. A.; Dzhemilev, U. M. *Reactions in Organic and Organometallic Synthesis*; NOVA Sci. Publ.: New York, 2010; p 96.
18. Tyumkina, T. V.; Islamov, D. N.; Parfenova, L. V.; Khalilov, L. M.; Dzhemilev, U. M. *Magn. Reson. Chem.* **2016**, *54*, 62–74. doi:10.1002/mrc.4311
19. D'yakonov, V. A.; Makhamatkhanova, A. L.; Tyumkina, T. V.; Dzhemilev, U. M. *Russ. Chem. Bull.* **2012**, *61*, 1556–1559. doi:10.1007/s11172-012-0205-4
20. Potapov, V. M. *Stereochemistry*; Chemistry, R. F.: Moscow, 1988.
21. Ibragimov, A. G.; Khafizova, L. O.; Satenov, K. G.; Khalilov, L. M.; Yakovleva, L. G.; Rusakov, S. V.; Dzhemilev, U. M. *Russ. Chem. Bull.* **1999**, *48*, 1574–1580. doi:10.1007/BF02496415
22. Kühl, O. *Phosphorus-31 NMR spectroscopy: a concise introduction for the synthetic organic and organometallic chemist*; Springer: Berlin, 2008.

License and Terms

This is an Open Access article under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/2.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The license is subject to the *Beilstein Journal of Organic Chemistry* terms and conditions:

(<http://www.beilstein-journals.org/bjoc>)

The definitive version of this article is the electronic one which can be found at:

doi:10.3762/bjoc.12.43